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Study of the changes in the structural and thermochemical behaviour of Nigerian De-oiled Physic nut (*Jatropha curcas* L.) Seed Kernel

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Abstract

Biobriquettes are a type of biofuel made from compressed organic waste materials such as agricultural residues, that are used for cooking, heating, and electricity generation. In this work, raw, hydrolysed (acid and alkali) and torrefied Jatropha curcas L de-oiled seed kernel were subjected to elemental, thermal, higher heating value (HHV), surface functional chemical groups (FTIR) and Scanning electron microscopy (SEM). The pulverized de-oiled J. curcas L. kernel (DJSK) was transformed to torrefied biomass through torrefaction within a temperature range of 200-300 °C under nitrogen ambience for 30 min. duration of residence. The atomic O/C and H/C ratios of the raw DJSK, torrefied

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raw DJSK, torrefied acid-hydrolysed DJSK and torrefied alkali-hydrolysed DJSK biomasses at 300 °C were 0.83, 0.12, 0.13, 0.13 and 0.16, 0.10, 0.07 and 0.07 wt % respectively. A decrease in O/C and H/C ratios were observed in the raw and pretreated biomass samples, upon torrefaction, which may be due to torrefaction temperature. Elemental analysis of the raw and pretreated biomass samples shows that at the second weight loss step, volatilization and burning of the volatiles occur between 150 °C and 500 °C, with a cellulose and lignin loses. The second stage pyrolysis is indicated as 332.4774 and 396.0412 wt % for DJSK. Increase in HHV were observed on both raw and hydrolysed samples as temperature rises from 200-300 °C. For the raw DJSK, the HHV were enhanced by factors of 1.00, 1.17 and 1.46 at 200, 250 and 300 °C and the same observation was detected in acid and alkali- hydrolysed samples. The spectra of the raw, acid and alkali- hydrolysed samples were similar. The stretching of the hydroxyl group, H-bonded (OH stretch) extended between 3200 and 3570 cm^{-1}. The absorption peaks at 2800 to 3000 cm^{-1} were allocated to Aliphatic C-H stretching in all DJSK samples and much more. The micrographs (via SEM) of the DJSK failed to exhibit any fiber-like compositions (woody biomass).

Keywords: *Jatropha curcas* L.; profitable utilization; torrefied biomass; torrefaction temperature; fuel wood.

INTRODUCTION

The fundamental needs (essentials) of the poor in developing nations are jobs, food, water, sanitation, transportation, healthcare, education etc. Energy plays a significant role in the provision of these services. The more available it is, the greater the consumption by human beings, including the poor masses. Energy, which is the basic ingredient for the delivery of necessary services for mankind such as lighting, transportation, heating and cooking, is mainly categorized into two forms: renewable and non-renewable. The request for the renewable energy consisting of biomass, solar, wind etc. has been growing rapidly over the past decades in the developing nations. Research into new ways of energy production is necessary because of global population growth (the population will reach 9 billion people by 2050) and the increase in hazardous emissions from fossil fuels (Lunguleasa *et al*., 2019). Most Nigerians living in rural areas depend exclusively on fuel wood (sawdust, firewood etc.) for their energy demands for the ages. At present, Nigeria consumes about 43 x 10^9 Kg of fuel wood with an average daily consumption ranging from 0.5-1.0 Kg of dry fuel wood per person annually for cooking and other domestic heating purposes (Onuegbu *et al*., 2010; Onochie *et al*., 2018). Similarly, the rate of consumption of woody products leads to generation of voluminous amounts of waste which are often discarded and burnt in unhealthy way (Akanni *et al*., 2019), thereby contributing to global warming. Biomass resources available in Nigeria include agricultural residues, animal waste, as well as energy crops etc. Efforts by the government of Nigeria to improve the resources management of biomass energy have essentially focused on enhancing the adoption of improved wood stoves, briquetting and biogas technologies (REMP, 2005). This is due to the fact that biomass energy is cheaper than the cost of energy derivable from non-renewable sources (e.g. liquefied petroleum gas and kerosene) and electricity.

Interestingly, global energy crises as well as high energy demands, depleting reserves, instability and fluctuating oil prices, environmental problems – pollution, global warming, climate change and impact on the ecology are the major concerns which necessitated prompt alternatives for the substitution of fossil fuels (Lateef *et al*., 2014a; Lee *et al*., 2017; Ogunsuyi *et al*., 2020; Lateef and Ogunsuyi, 2021a). With a view to mitigate the global repercussions of climate change, there is compelling need to lower carbon emissions significantly worldwide, or possibly zero emission. Many countries have acknowledged the need to divert from fuels derived from coal, oil and natural gas to renewable energy as a means to attain this; because energy from renewable sources is infinite and could be quickly replenished. Meanwhile, the non-renewable nature of fossil hydrocarbons means that fuel pools are finite; because as new oil fields are set up, the older ones get depleted. Nigeria, an energy rich nation with significant abundance of solar, wind, hydro and biomass etc., is equally blessed with fossils –such as crude oil, natural gas and coal. Among all these renewable energies, supplying heat, power and chemicals, biomass is considered plentiful, inexpensive, and is regarded as the only renewable resource supplying liquid, gaseous, solid fuels and commodity chemicals (Iliopoulou *et al*., 2018); therefore, full utilization of lignocellulose is vital for the cost effective production of bioproducts (biofuels, biochemical etc.) (Satyavolu *et al*., 2021). Biofuels are fuels produced from biomass. Biofuels synthesis from biomass feedstocks are renewable, biodegradable, readily available and environmentally benign resources (Lateef *et al*., 2018). Biomass depicts the most encouraging renewable energy resources and is regarded to be a feasible alternative to fossil fuels (Ahamed *et al*., 2011).

Generally, biomasses are inherently complex and heterogeneous in composition and can be non- responsive or uncooperative to conversion reactions (Champagne *et al*., 2010; Lateef and Ogunsuyi, 2021b). Lignocellulosic materials (biomass) comprises of three types of polymers, namely cellulose, hemicellulose and lignin which are related with each other (Chen *et al*., 2018). With a view to magnify the digestibility of biomass, pretreatment is mandatory. Pretreatment methods include (i) mechanical (e.g milling) (ii) thermal (e.g steam pretreatment/ steam explosion) (iii) acid (dilute or strong acid – e.g sulphuric or nitric acid) (iv) alkali (e.g sodium or potassium hydroxide (v) oxidative (oxidizing compound e.g hydrogen peroxide or peracetic acid) (vi) combinations, ammonia and carbondioxide. Of all these, alkali and acid pretreatments can be performed continuously and at low cost, compare to other methods which are more expensive (Hendriks and Zeeman, 2009). For the purpose of surface morphology studies using scanning electron microscope (SEM), it is important to discuss the effect of acid and alkaline pretreatments on both raw and torrefied biomass.

Diluted or concentrated acids can be employed to achieve acid pretreatment. Organic and inorganic acids including H_2SO_4, HCl, HNO_3, H_3PO_4, acetic acid and maleic acid have all been utilized for acid pretreatment, with H_2SO_4 being the most frequently used acid (Den *et al*., 2018). H_2SO_4 (generally 1-4 wt %) (Galletti and Antonetti, 2011) is the most regularly employed acid: a logical mild acid pretreatment solubilizes part of the hemicellulosic constituent of the biomass and exposing a larger area of cellulose (at low acid concentration) to enzymatic attack (Guilherme *et al*., 2017). In dilute acid hydrolysis, the firm structure of the lignocellulosic materials is broken, succeeded by the removal of hemicelluloses, thereby accelerating the porosity and digestibility of biomass (Badiei *et al*., 2013; Lateef and Ogunsuyi, 2021b). In industries, it is important to stress that dilute or concentrated acid are more dangerous and most corrosive for reactors and equipments, therefore the acid must be retrieved after the pretreatment (Galletti and Antonetti, 2011).

As compared to acid hydrolysis, alkaline hydrolysis employs alkaline solutions. The method demands alkaline solution of sodium hydroxide, calcium hydroxide or ammonia for the pretreatment of biomass (Kumar *et al*., 2015). The two most popular alkali are the Sodium hydroxide and lime. Alkaline pretreatment amplifies porosity and internal surface area by aiding structural swelling, decreases degree of polymerization and crystallinity, thus breaking down the lignin structure (Den *et al*., 2018). Lignin is set apart from inhibitors through neutralization (Badiei *et al*., 2013). Alkaline hydrolysis process implies modification in the structure of lignin, as well as partial decrystalization of cellulose and partial solvation of hemicellulose (Galletti and Antonetti, 2011; Badiei *et al*., 2013). Sodium hydroxide has been widely studied for many years and it has been shown to significantly disrupt the lignin structure of the biomass, with many successful report on corn stover, switchgrass, bagasse, wheat and rice straw (Kumar *et al.*, 2015). Another important aspect of alkaline pretreatment is the change of the cellulose structure to a form that is denser and thermodynamically more firm than the native cellulose (Hendriks and Zeeman, 2009). The conditions for alkaline pretreatment are usually less drastic than other pretreatment as it involves soaking the biomass in alkaline solutions and mixing it at a target temperature for a definite amount of time (Badiei *et al.*, 2013; Kumar *et al.*, 2015). The pretreatment can be achieved at low (0.5-4 wt % NaOH) or at high (6-20 wt % NaOH) concentrations; at low NaOH concentration, the pretreatment targets at lignin and hemicellulose removal and is executed at higher temperature and atmospheric pressure (Den *et al.*, 2018) usually at ≥ 120 °C with biomass particle size ≤ 2 mm for 30 min. (Guilherme *et al.*, 2017).

The high, quality and reasonable oil content in *Jatropha curcas* L. biomass is the chief driver of biodiesel production from this biomass all over the world. Biodiesel extracted from plant oil is an alternative renewable fuel source reducing dependence on fossil fuels (Sotolongo *et al.*, 2007; Lateef *et al.*, 2014a). This is achieved through the process called transesterification (Ogunsuyi, 2012; Lateef *et al* 2014b). A plant deserving a great deal of attention for biodiesel production is *Jatropha curcas* L. (Lateef *et al.*, 2014b; Lateef, *et al.*, 2014c). *Jatropha curcas* L. is a non-edible oil bearing, drought resistant, hardy shrub with ecological advantages; belonging to the family – Euphorbisceae (Singh *et al.*, 2008). There has been intense effort in *Jatropha curcas* L. processing research, focusing mainly on waste valorization (in developed nations), since these waste are very low in cost, abundant, readily available and renewable (Champagne *et al.*, 2010). There are various processes or the combination of processes to obtain oil from oil-bearing plants. These are Mechanical extraction, conventional solvent extraction and Supercritical fluid extraction (Lateef *et al.*, 2014b; Nde and Foncha, 2020). Taking Economics into consideration, mechanical extraction is considered to be the most promoted because of lower operational cost, even though solvent oil extraction gives higher oil yield (Gan *et al.*, 2019). According to Olajide (2007), mechanical oil extraction produces relatively good quality oil and it permits for the use of the cake residue.

Apart from biomass complexity and heteregeniousity in nature, biomass is identified by its high moisture content, low calorific value, hygroscopic nature and larger volume or low bulk density and therefore several methods have been advanced to improve biomass conversion effectiveness (Chen *et al.*, 2011). One of such important method to overcome aforementioned problems is torrefaction. Torrefaction, (also referred to as mild pyrolysis) involves the biological, chemical, and thermal breakdown of biomass. Torrefaction is stated as the thermochemical process in an inert ambient, whereby biomass is gradually heated in a specific range of temperature between 200 and 300 °C, under an atmospheric pressure and characterized by a low heating rates of particle (< 50 °C) within a time less than 60 min. (Ahmad *et al.*, 2017; Grycova *et al.*, 2020). Generally, torrefaction is the low temperature pyrolysis and the main purpose in the torrefaction process is to decrease the humidity of the biomass and increase its higher heating value (Aamiri *et al.*, 2019; Duranay *et al.*, 2019). After torrefaction, the product yielded are reported to be of low in moisture contents, hydrophobic, higher heating value, high energy density, improved grindability (if in bales), non-biodegradable (Acharya *et al.*, 2015) and can be stored safely over time with little risk of mold. Torrefied biomass, when densified finds application as second generation wood pellet of comparable quality to substitute thermal coal and metallurgical coal in power plants and blast furnances (Chen *et al.*, 2015).

In Nigeria, wood dust (popularly called sawdust) is a by-product of woodworking operations such as sawing, milling etc. and is frequently used in many rural homes as an alternative domestic fuel. However, the wood dust is used as fuel in its raw form with the enormous release of volatiles, smokes and soot and this reduces its prospects and satisfactoriness as an alternative energy material (Lateef and Ogunsuyi, 2021a). Nigeria generates about 1.8 million tons of sawdust annually and 5.2 million tons of wood waste (Owoyemi *et al.*, 2016). However, despite the wood dust upgrading through briquetting and the development of improved wood stoves by the Energy commission of Nigeria, little or no success was recorded, as regards its impact on the higher heating value (Lateef and Ogunsuyi, 2021a). Torrefied biomass could be substituted for wood dust for domestic heating and cooking purposes. Publications on biomas torrefaction are limited in Nigeria compare with advanced nations where this technology is embraced. Therefore, there is need for Energy commission of Nigeria to focus on this engineering initiative to convert the huge amount of unused or discarded biomass to torrefied biomass (which can as well be pelletized or briquetted) that has proven to have higher heating value than the raw biomass for cooking and heating purposes for both rural and urban dwellers.

In reviewing researches on lignocellulosic biomass torrefaction globally, it can be found that most of the studies are concerned on proximate, fiber, elemental and calorific (Higher Heating Value) analyses (Chen *et al.*, 2011); effect of torrefaction on chemical and physical properties e.g FTIR spectroscopy, thermogravimetric analysis, scanning electron microscopy (Doshi *et al.*, 2014). So far, there is little or no report on the effect of chemical pretreatments (- acid and alkaline) on the physical and chemical properties (elemental, thermal, higher heating value (HHV), surface functional chemical groups (FTIR) and Scanning electron microscopy (SEM)) of Jatropha biomass waste. Lastly, a look at the literature in Nigeria (to the best of our knowledge) shows that little, or not much work has been done to valorise Jatropha waste biomass feedstocks in the area of solid fuel production in peer-review open access journals. Consequently, with expansive waste emanating from *Jatropha curcas* L. biomass after oil extraction for biodiesel production; the neglected wastes can be utilised as energy material for pellets or briquettes formulation which can aptly serve as substitute domestic fuel. Many thermochemical conversion processes such as torrefaction, pyrolysis, gasification etc. have been published in literature as a respectable approach for increasing the fuel properties of waste biomass. Therefore, this study would provide not only baseline data but also ensure non-zero waste of the de-oiled *Jatropha curcas* L. seed kernel after oil extraction.

MATERIALS AND METHODS

Sample collection

The selected biomass - semi-dried *Jatropha curcas* L. fruits fully grown to a dark-brown condition were purchased and harvested manually from Jatropha plantations in Idah, Kogi State, Nigeria and transported to the Department of Chemistry, The Federal University of Technology, Akure, Ondo state. Extraneous materials were handpicked and discarded.

Sample preparation

Each seed was separated from the fruit hull and sun-dried for a period of 30 days. The shells were manually separated from the seed kernels. The remaining Kernels were ground into fine powder with grinding machine (6.5 HP, Japan). The milled kernel was mashed exposed to moisture conditioning pre-treatment as described by Subroto *et al.* (2015) for mechanical oil exraction. The recovered cakes were kept in and air tight container and preserved for further use. For the analysis, analytical grade reagents were used as received.

Pretreatment of Biomass feedstock

J. curcas L. biomass feedstock pretreatment were carried out in a representative engineering scale (reactor) for both acid and alkaline hydrolyses of *Jatropha curcas* L. biomass sample as described in Lateef and Ogunsuyi (2021a)

For acid hydrolysis of the bioma**ss,** the DJSK biomass was immersed separately in 4 % sulphuric acid solution and exposed to heating at a temperature of 109 °C for 30 min (Tutt *et al.*, 2012) modified. Furthermore, the acid-pretreated biomass was bathed thoroughly with tap water; 0.1 M sodium hydroxide was added to neutralize the acid and agitated thoroughly with tap water until pH adjusted to 7.0.

The alkaline pretreatment was carried out using 4 wt. % sodium hydroxide solution (Guilherme *et al.*, 2017) modified. The biomass feedstock DJSK were immersed in a 4 wt. % sodium hydroxide solution and subjected to heating at 109 °C (followed by intermittent shaking) for 30 min. The pretreated biomass was washed thoroughly; 0.005 M of H_2SO_4 was introduced to neutralize the base, stirred thoroughly with tap water until neutral (pH adjusted to 7.0). For details, the reference method used for alkaline hydrolysis is contained in Lateef and Ogunsuyi (2021b).

Torrefaction Set-up

A bench-scale fixed bed reactor (torrefaction device), which was developed and as described in Lateef and Ogunsuyi, 2021a. The device consists of the following components: Casing design system, Refractory system, Heating system, Temperature controller and Contactor, and Safety system. A 50 g of the sample was flushed with nitrogen gas at 0.5 bar for 3 min. The biomass samples were torrefied in a nitrogen atmosphere at 200, 250 and 300 ^{0}C for 30 min. (Kopczynski *et al.*, 2015) residence time. The torrefied biomass in the reactor was left to cool to ≤ 60 ^{0}C after which it was taken out and weighed. The cooled torrefied biomass was stored in an air-tight containers and were taken for analyses. Detailed description of the Torrefaction experimental set-up is as described in our previous studies (Lateef and Ogunsuyi, 2021a).

The solid yield, enhancement factor and energy yield of the samples were determined as described in Lateef and Ogunsuyi (2021a).

Elemental Analysis

Elemental analysis of the raw and severely torrefied biomass pulverized and sieved samples (USA standard sieve ASTM E-11 standard no 140 Cole-Palmer, USA) were carried out by Elemental Analyzers for CHN (Elemental Analyzer, Exeter CE-440, USA) and the oxygen analysis was determined using Thermolyn Combustion Furnances setup to provide total oxygen weights through Gas Chromatography.

Thermal Analysis

Simultaneous Differential Scanning Calorimetry/ Thermogravimetric Analyzer (DSC-TGA SDT Q600 from TA instruments) was used for the thermal analysis to measure both heat flow and weight changes of the biomass precursors as a function of temperature over a temperature range of 30-600 °C. The DSC-TGA tests were used to further understand the thermal behaviours of biomass precurcors before pyrolysis and torrefaction. It is a ramp up method. The heating rate and flow rate was measured at 10 °C/min (in a nitrogen atmosphere) and 100.0 ml/min respectively. Testing conditions: carrier gas speed: 15ml (Hc)/min; quantity of biomass sample: 13.40 mg (DJSK). All DSC-TGA tests were performed in triplicate.

Determination of Higher heating/Calorific value

The estimation of Calorific values was achieved using e2k calorimeter (model: Crl001). A mass sample of 0.5g was weighed on the 2 cm firing cotton strapped to the firing wire on the lid assembly and positioned inside the metal crucible. The lid assembly was then placed inside the bomb air-tight as described by Lateef and Ogunsuyi (2021a).

FTIR Analysis of Raw and Torrefied Samples

The FTIR spectra of the biomass samples were acquired by using PerkinElmer, FTIR spectrum BX II. About 2 mg of the biomass was well mixed with 200 mg of ground KBr and the mixture was compacted for preparation of pellets. Each spectrum was the mean of 64, co-addition of scans with a total scan time 15 seconds in the IR range of 400 – 4000 cm^{-1} at 2 cm^{-1}.

SEM analysis of raw and torrefied samples

The morphological characterization of raw and torrefied *Jatropha curcas* L. biomass were assesed by electron microscope (SEM, JSM-6390LV, 6733B-IUUS-SN, Thermo Electron Corporation, USA) assembled with an energy dispersive X-ray (EDX) Spectrometer and X-max detector (Oxford-instruments, INCA 400, UK). The samples were placed on the SEM stub using double-side carbon tape, placed into the chamber controlled at about 1.4 x 10^{-3}, 15 kV accelerating voltage, 5 – 100 µm working distances and 50- 5,000 times magnification.

RESULTS AND DISCUSSION

Elemental Analysis

Elemental analysis of the raw and pretreated biomass samples are as given in Table 1

Table 1: Elemental Analysis of *Jatropha curcas* L. biomass samples

Biomass sample	Elemental compositions (wt %)					
	C	H	N	O	O/C	H/C
RawDJSK	16.27	2.58	1.82	13.56	0.83	0.16
Torrefied raw DJSK @ 300 °C	55.41	5.80	6.55	6.73	0.12	0.10
Torrefied acid hydr. DJSK @ 300 °C	50.11	3.52	8.83	6.73	0.13	0.07
Torrefied alkali hydr. DJSK @ 300 °C	50.96	3.52	8.82	6.72	0.13	0.07

*hydr. represents hydrolysed

Torrefaction process temperature may likely be responsible and attribute for the decrease in O/C and H/C ratios as observed in the raw and pretreated biomass samples. The atomic O/C and H/C ratios of the raw DJSK, torrefied raw DJSK, torrefied acid-hydrolysed DJSK at 300 °C and torrefied alkali-hydrolysed DJSK biomasses at 300 °C were 0.83, 0.12, 0.13, 0.13 and 0.16, 0.10, 0.07 and 0.07 wt % respectively. According to Duranay and Cayci (2019); an increase in torrefaction process temperature causes reduction in hydrogen and oxygen content; which leads to increase in the carbon content thus enhancing the fuel properties of the torrefied biomass. Again, with increase in torrefaction temperature during biomass combustion; water, carbondioxide, as well as low molecular weight components are expected to be released from the biomass feedstoock via the process of devolatilization. Similar observations were noticed in the pretreated feedstock for all the biomasses.

Similarly, the O/C and H/C ratios of the raw (untorrefied) acid and alkali pretreated biomass samples are higher than the raw (torrefied) and the pretreated torrefied samples. The raw DJSK biomass sample has a higher O/C ratio 0.83 wt % than the acid-hydrolysed and alkali-hydrolysed torrefied samples 0.13 wt %. Therefore, it is obvious that the O/C of the raw DJSK is comparatively greater than the raw (torrefied) and pretreated torrefied biomass samples.

Evidently, the oxygen in both the raw (torrefied) and pretreated (torrefied) samples subsided because cellulose and hemicellulose were consumed and this consumption was more pronounced than lignin. Similar observation was made by Ahmad *et al.*, (2017), on the evaluation of pulverized biomass property for solid fuel through torrefaction. This could be explained that thermochemical biomass temperature and pretreatment has a great effect on biomass elemental analysis. For example, biomass elemental composition without pretreatment, has high oxygen content; whereas when biomass is pretreated and torrefied, the oxygen content dropped dramatically. A profound look at Table 1 showed that, on account of pyrolytic character of torrefaction, partial oxygen reserved in the biomass was engaged for thermal degradation (causing visible changes in biomass physical properties), as could be deduced from changes in weight percentages between the raw (untorrefied) and raw (torrefied) as well as pretreated biomass samples.

Thermal Analysis

Elemental analysis of the raw and pretreated biomass samples are displayed in Fig.1.

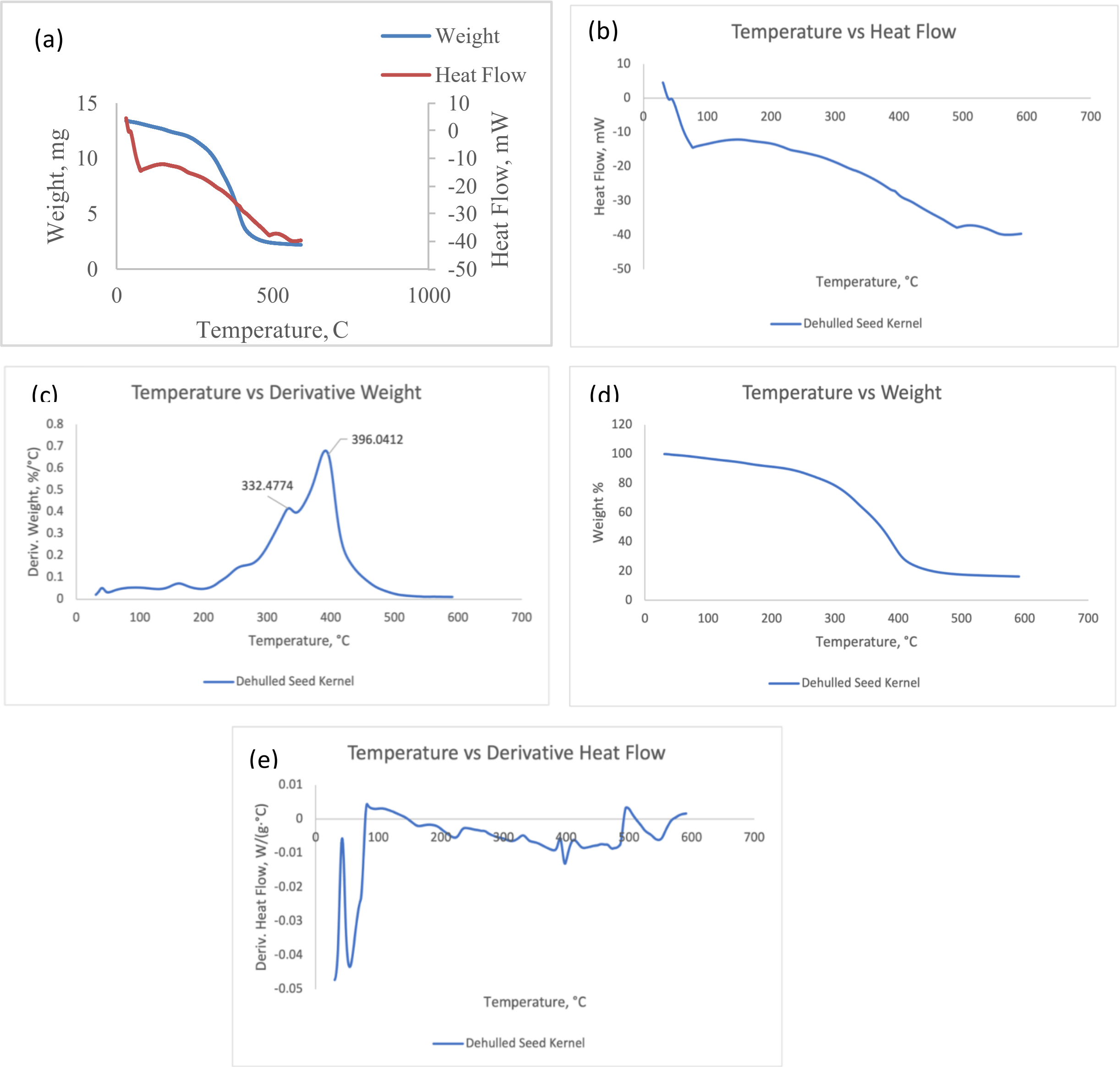

Fig. 1. DJSK (a) Simultaneous DSC-TGA curves at 10 °C/min. (b) Temperature vs heat flow (c) Temperature vs derivative heat flow (d) Temperature vs weight (e) Temperature vs derivative weight

Fig. 1 shows the simultaneous DSC-TGA curves for the DJSK biomass sample. Using the TGA curves, the pyrolysis process can be apportioned into three major stages: moisture evaporation, main devolatilization and continuous slight devolatilization (Ounas *et al*., 2011). Generally, the thermal degradation characteristics of the biomass samples are distinguished via three-stage thermal degradation, putting in mind that thermal decomposition of these biomass feedstocks occured in the second stage. From the TGA curves, it can be seen that the sample moisture removal (dehydration) was indicated at about the margin of 150 °C for the DJSK biomass. The first weight loss step between the room temperature (30 °C) and 300 °C, indicating loss of volatiles, moisture, oil, solvents etc. At this stage, the sample pyrolyses in a single step. Generally, there are three main stages of thermal degradation: drying (stage 1), active pyrolysis (stage 2), and passive pyrolysis (stage 3) (Henne *et al*., 2019). At the second weight loss step, volatilization and burning of the volatiles occur between 150 °C and 500 °C, with a cellulose and lignin loses. The second stage pyrolysis is indicated as 332.4774 and 396.0412 wt % for DJSK. Passive pyrolysis takes effect from above 500 °C where massive mass loss was experienced. The crucial weight loss transformation takes place between 200 and 380 °C. Similarly, the terminal weight loss transition from 400 °C to 550 °C was minor for all the biomasses. These observations as regard TGA in *Jatropha curcas* L. biomass precursors is consistent with the reports of the earlier studies (Pyramides *et al*., 1995; Lu *et al*., 2013; Doshi *et al*., 2014; Lateef and Asadu, 2018).

Higher Heating Value (HHV)

The HHV of the raw and pretreated DJSK are shown in Table 2.

Table 2: Higher Heating Value (HHV) of Torrefied/ Raw and hydrolysed DJSK Biomass

Biomass	HHV (MJ/Kg)
Raw DJSK	23.20
Acid hydrolysed DJSK	25.39
Alkali hydrolysed DJSK	21.93

The HHV of the biomass was greatly enhanced by the acid pretreatment. The raw biomass as received after sun drying had a lower higher heating value than the acid-treated DJSK. Acid-treated DJSK had a greater HHV (25.39 MJ/Kg) than raw DJSK (23.20 MJ/Kg). This may be as a result of the fact that generally, acid pretreatment brings about effective hydrolysis of cellulose and hemicellulose and changes lignin structure. Hsieh *et al*., (2015), made a similar observation in their work, where the HHV of the untreated rice straw biochar had 18.30 MJ/Kg HHV and increased to 21.00 MJ/Kg when acid pretreated with 5 % HCl. It is equally observed that the HHV of alkali-treated DJSK possessed a lower heating value of 21.93 MJ/Kg than the untreated DJSK. Generally, alkali hydrolysis leads to lessening or removal (regulated by the concentration of the alkali used) of lignin and hemicellulose, thereby increasing the available surface area. The significant drop in the HHV 21.93 MJ/Kg of alkali-treated DJSK may be ascribed to the partial saponification reaction, whereby the NaOH alkali-treatment hydrolyses/washes off some of the oil in the parent biomass, that is DJSK which might have contributed to its high heating value. The HHV of raw and treated DJSK were higher than the calorific power of non-thermal treated sawdust biomass for some wooden species from southeast Europe- 18.02, 18.05, 17.98 and 17.63 MJ/Kg for spruce, larch, oak and beech respectively; and this increased continuously during torrefaction up to 20.58 MJ/Kg (14.1 % increase), 20.71 MJ/Kg for larch (11.8 % increase), 20.94 MJ/Kg for oak (16.4 % increase) and 21.30 MJ/Kg for beech (20.7 % increase) (Lunguleasa *et al*., 2019). The higher heating value of the raw and pretreated DJSK reported in the work is higher than the 19.58 MJ/Kg reported for raw sawdust from *Alstonia congenesis* Engl woody biomass sawdust of Nigeria origin (Oyebode and ogunsuyi, 2021). The HHV reported for DJSK goes a long way to affirm the suitability of de-oiled DJSK as a suitable replacement for sawdust considered as a source of fuel for cooking in developing nation like Nigeria.

Effect of torrefaction temperatures on Solid yield, Enhancement factor, HHV and Energy yield (%)

The solid yield (%) for the raw and pretreated DJSK biomasses (dilute acid and mild alkali at 4%), enhancement factor (%) and energy yield (%) at different torrefaction temperatures of between 200-300 °C, 1.14 mm particle size, 30 min. torrefaction residence time are presented in Table 3.

Table 3: DJSK biomass HHV, Solid yield, Energy yield (%) and enhancement factor

Temperature (^{0}C) 30 min, 1.14 mm	Raw DJSK	Acid-treated DJSK	Alkali-treated DJSK
HHV			
200	23.277	26.164	22.004
250	27.146	26.237	22.646
300	27.279	26.813	23.200
Solid yield (%)			
200	70.00	28.00	34.00
250	33.20	25.00	25.00
300	30.00	12.00	21.00
Enhancement factor (%) of HHV			
200	1.00	1.03	1.00
250	1.17	1.03	1.03
300	1.18	1.06	1.06
Energy yield (%)			
200	70.00	28.84	34.00
250	38.84	25.75	25.75
300	35.40	12.72	22.26

As can be seen in Table 2 above, Increase in HHV is observed as temperature rises from 200 °C to 300 °C. For the raw DJSK, the HHV are enhanced or enlarged by factors of 1.00, 1.17 and 1.46 at 200, 250 and 300 °C. Same observations were noticed in acid and alkali treated samples. With increase in reaction temperature, the solid yield (%) of both raw and treated (acid and alkali) sample decreased. At 200 °C, the decrease in solid yield was brought about by the elimination of low molecular weight aromatic compounds, as well as partial degradation of lignin. When the torrefaction temperature was increased to 250 and 300 °C, an evident mass loss of the samples was noticed which was attributed to breakdown of hemicelluloses and partial decomposition of cellulose and lignin as well as the liberation of the corresponding products (Li *et al.*, 2018). Even though, the HHV of biomass increased as temperature rises, the weight loss at the higher torrefaction temperature is also pronounced. Carbonisation of biomass during torrefaction led to the reduction in moisture content and increase in HHV, hence making the biomass energy dense (Oyebode and Ogunsuyi, 2021); meaning, the observed decrease in moisture content of the biomass has positive influence on the carbon content of the biomass. This relationship is inversely proportional; as the torrefaction temperatures increase, the moisture content is reduced, while the carbon content and HHV increases. The solid yield for the raw DJSK at 300 °C is 30 % which is far less compared to 70 % of the same biomass torrefied at 200 °C. It follows that temperature has a marked effect and that the more the torrefaction temperature increases, the less the solid yield and vice-versa.

Moreover, the energy yield (%) decreases as torrefaction temperature increases for both raw and treated samples. For e.g., taking the raw DJSK as the basis, at torrefaction temperature of 200 °C, the energy yield or the total energy retained in torrefied biomass is 70 %, but with the torrefaction temperature increased to 250 °C, the total energy retained in the biomass decreased to 38.84 % and subsequently to 35.40 % at 300 °C respectively. According to Chen *et al*., (2011), the magnified HHV from torrefaction is inadequate to counteract the weight loss of biomass and as a result, a monotonic drop in the total energy ratio with accelerating torrefaction temperature is revealed. In addition, the diminishing propensity in the energy yield is far more severe in acid-treated biomass than both raw and alkali-treated DJSK.

FTIR SPECTRA ANALYSIS

The FTIR spectra of raw (untorrefied) and torrefied DJSK and its corresponding torrefied acid-treated DJSK and torrefied alkali-treated DJSK are shown in Figs.2-4 with the bands of interest being distinguished by their wavenumbers. The band assignments of the spectra are as contained in biomass torrefaction reports (Tjeerdsma *et al*., 1998; Bustin and Guo, 1999; Chen *et al*., 2008; Kleber *et al*., 2010; Park *et al*., 2013; Kikuchi *et al*., 2014; Acharya *et al*., 2015; Kopczynski *et al*., 2015; Ahmad *et al*., 2017).

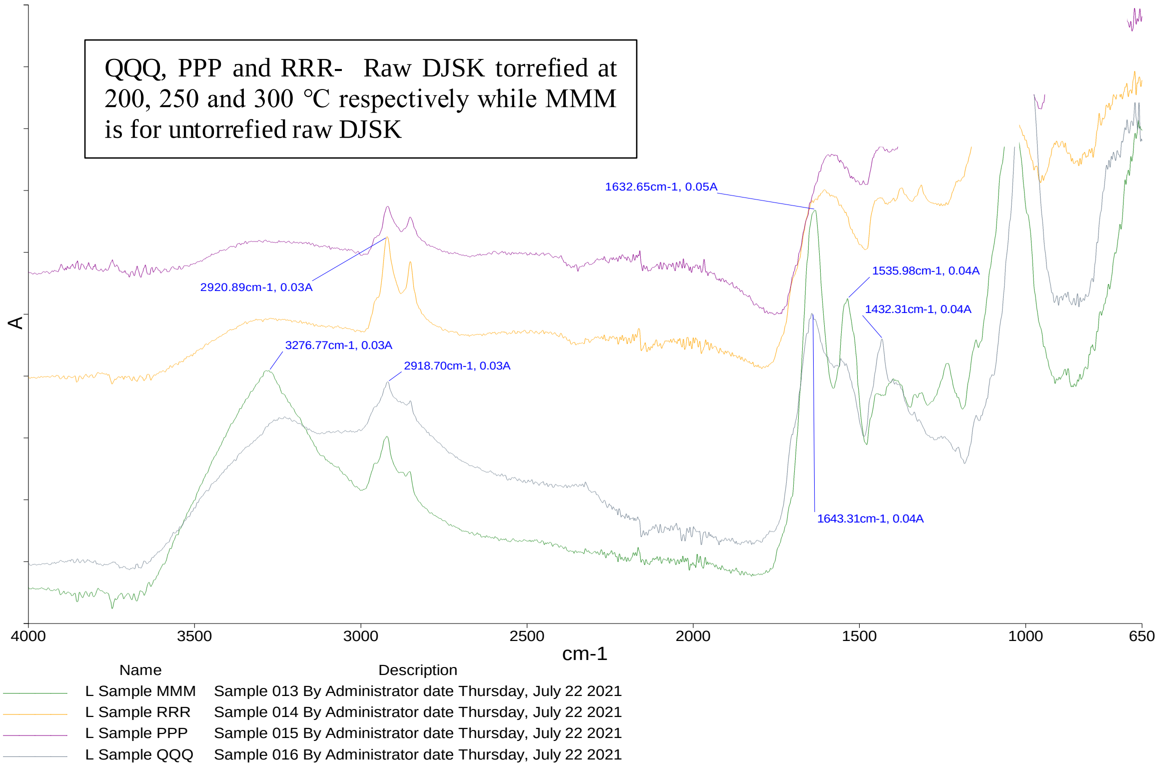

Fig 2: FTIR spectra for untorrefied and torrefied raw DJSK at 200, 250 and 300 °C

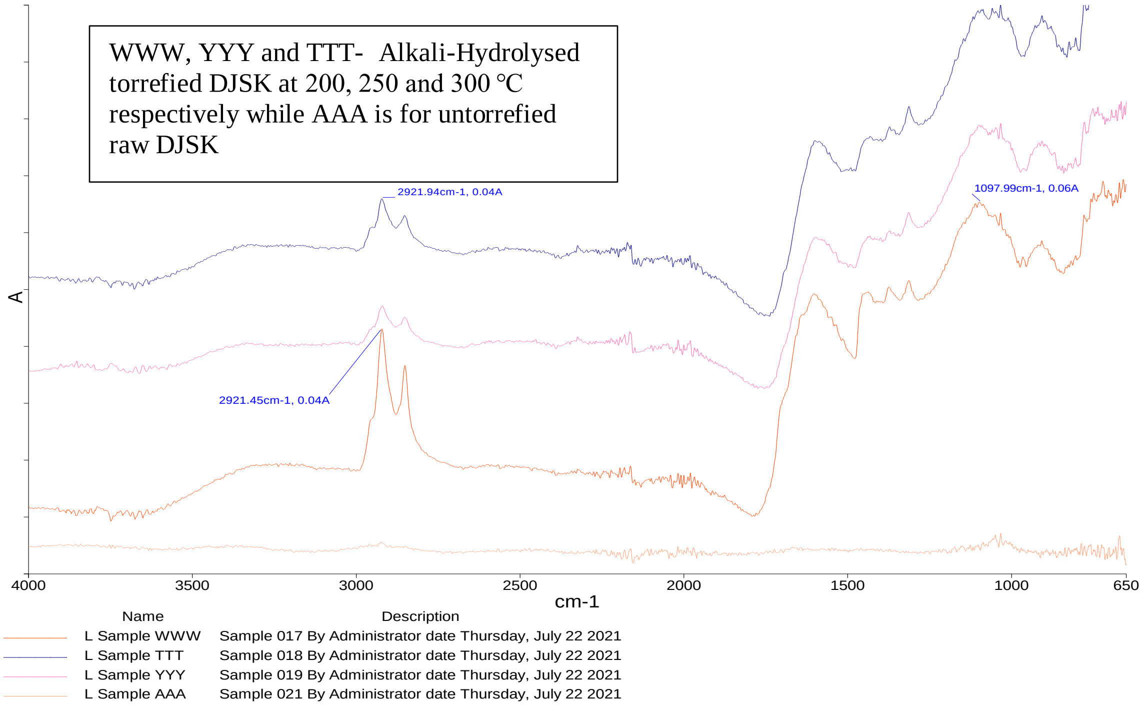

Fig 3: FTIR spectra for untorrefied and torrefied alkali hydrolysed DJSK at 200, 250 and 300 °C

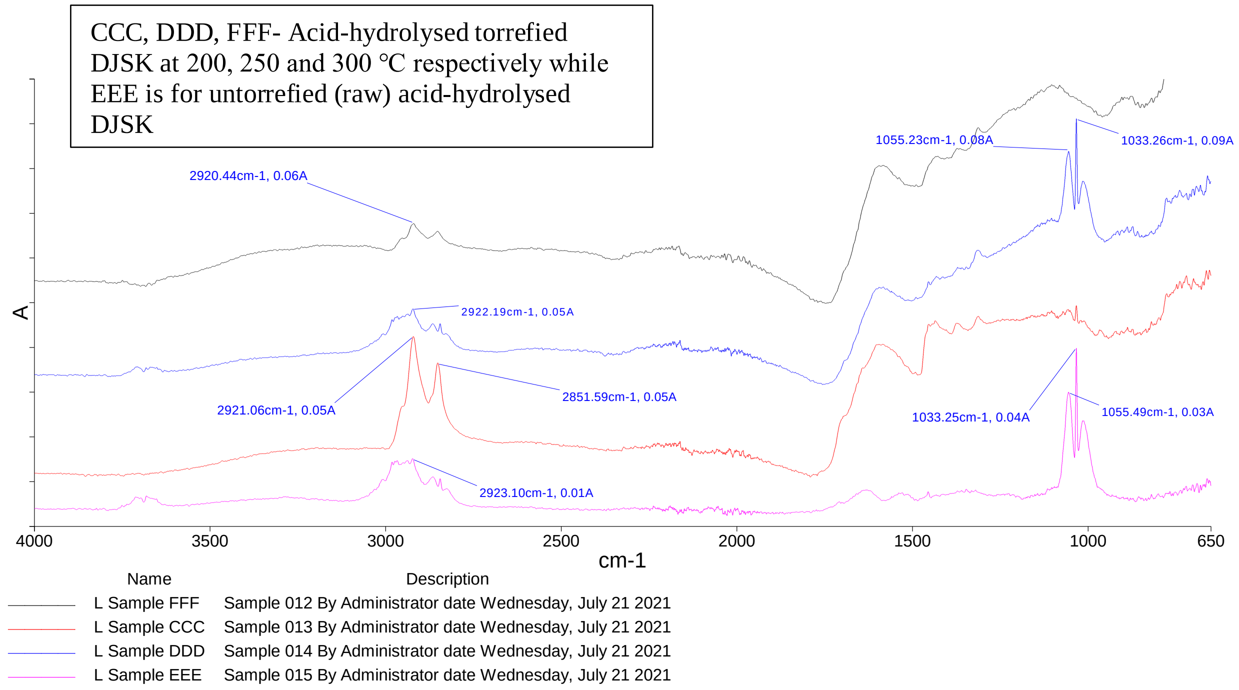

Fig 4: FTIR spectra for untorrefied and torrefied acid-hydrolysed DJSK at 200, 250 and 300 °C
FTIR spectra of (a) untorrefied (raw) DJSK; (b) torrefied DJSK, (c) torrefied acid-hydrolysed DJSK and (d) torrefied alkali-hydrolysed DJSK

The FTIR studies of the mechanically de-oiled (raw) and the pretreated (acid and alkali-hydrolysed) torrefied and untorrefied DJSK are shown in Figs. 2-4. The spectra of the raw, acid and alkali- hydrolysed samples are similar. The stretching of the hydroxyl group, H-bonded (OH stretch) extended between 3200 and 3570 cm^{-1} (Coates, 2006). According to Wu *et al.*, (2012), the presence of 1 % moisture may be responsible for he the hydroxyl group present in the raw and hydrolysed biomass samples. Furthermore, Wu *et al.*, (2012), suggested that once biomass torrefaction temperature goes beyond 300 °C, the biomass feedstock hydroxyl group (-OH) is destroyed, thereby enhancing biomass capability to lose its capacity to form hydrogen bonds with water, thereby changing the hygroscopic nature of the biomass to hydrophobic. Also distinguishable prominent peaks are between 2927.03 and 2928.51 cm^{-1} in the raw (untorrefied) acid and alkali-hydrolysed DJSK. According to Shang *et al.*, (2012), these bands disappeared in the torrefied samples. Till date, no scientific empirical evidence has been given to support this disappearance. The absorption peaks at 2800 to 3000 cm^{-1} were allocated to Aliphatic C-H stretching in all DJSK samples. These bands appear not to change remarkably due to the heat treatment of torrefaction (Shang *et al.*, 2012) and the extracted biomass at these peaks indicate the loss of aliphatic carbon and carboxylic group (Tjeerdsma *et al.*, 1998; Lateef and Asadu, 2018). The peaks between1300-1500 cm^{-1} indicates Aliphatic C-H deformation (Meeyoo *et al.*, 2007). The peaks between 1000 and 1100 cm^{-1} is ascribed to C-O stretching of carbohydrate, manifesting the existence of polysaccharides or cellulose; as these could be found in torrefied raw DJSK at 300 °C and torrefied alkali-hydrolysed DJSK at 200 °C. These peaks appear in the raw and torrefied acid-hyrolysed DJSK at 300 ^{0}C (1048.13, 1087.30 and 1097.99 cm^{-1}) respectively. Similar observation was noticed in the torrefied acid-hydrolysed DJSK at 250 and 300 ^{0}C (1055.23; 1033.00, 1055.49 cm^{-1}) respectively. These peaks are cellulose structure belonging (Lateef, and Asadu, 2018; Gan *et al.*, 2019) and it decreases from raw sample and as torrefaction temperature increases (Park *et al.*, 2013); indicating the loss of carbohydrate, as well as dehydration and decarboxylation of carbohydrates in the sample (Gan *et al.*, 2019).

Surface Morphology

There were some visible changes in the surface morphology of raw, pretreated (hydrolysed) pulverized Jatropha biomass waste DJSK biomass. SEM was used to gain a deeper understanding of the impact of torrefaction on the surface morphology of the raw, pretreated (hydrolysed) pulverized Jatropha biomass waste with particle size 1.14 mm, torrefaction duration of 30 min. as shown on Figs. 5-7.

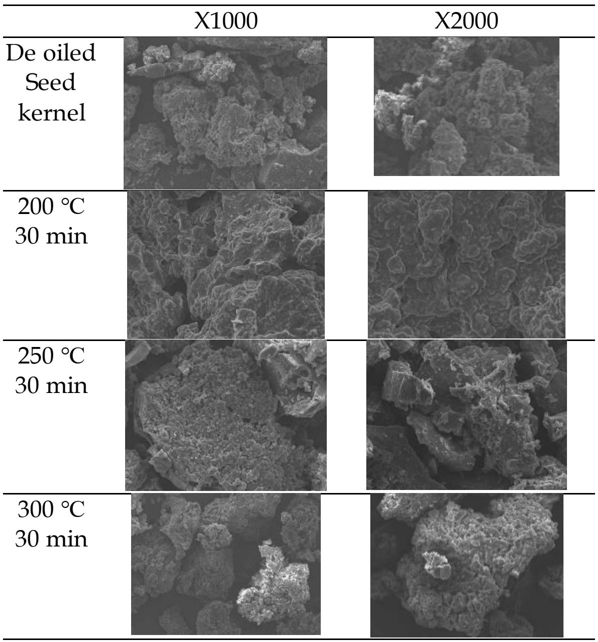

Fig. 5: SEM image of untorrefid DJSK and torrefied DJSK at different temperatures (200, 250 and 300 °C)

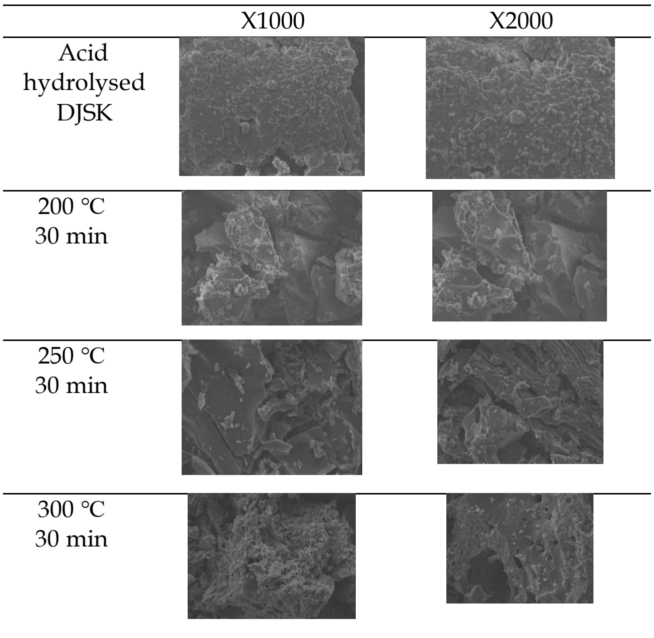

Fig. 6: SEM image of untorrefid acid-treated DJSK and ttorrefied acid-treated DJSK at different temperatures (200, 250 and 300 °C)

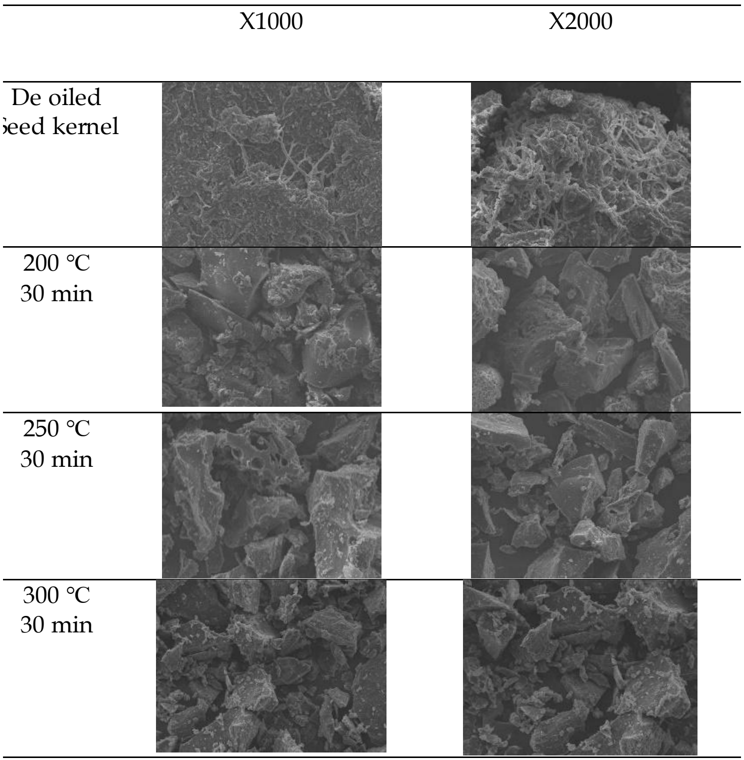

Fig. 7: SEM image of untorrefid alkali-treated DJSK and ttorrefied alkali-treated DJSK at different temperatures (200, 250 and 300 °C)

According to Hidayat *et al.*, (2014); SEM micrographs of the DJSK do not exhibit any fiber-like structures (woody biomass). The kernel (both treated and untreated) is distinguished by a cellular structure with thin walls and intercellular spaces. For the raw DJSK as in Fig. 5, the microparticles on the surfaces can be distinctly observed. The microparticles are obvious on the untorrefied DJSK. Temperature has a profound effect on the surface morphology of biomasses. Torrefied biomass at 200 °C of DJSK did not have much impact on the microparticles. But at 250 °C, the microparticle diminishes. This observation is in agreement with Satyavolu *et al.*, (2021); that increasing torrefaction temperature consumes more tiny particles and improves the impact of thermal pretreatment on the biomasses. He posited that the decrease in microparticles was largely due to decomposition of the hemicelluloses and non cellulose, leading to damaged surface. Hemicellulose is the most reactive constituent of biomass and it is ascribed to the substantial mass loss in biomass during torrefaction (Acharya *et al.*, 2012). As the torrefaction temperature built up to 300 °C, the microparticles decreased significantly. This goes in proving that DJSK is a susceptive biomass to torrefaction; because as the temperature increases, hemicelluloses and non cellulose are consumed from the specified torrefaction temperature and therefore, at 300 °C, porous structure are clearly observed. The acid and alkali pretreatment enhanced the surface structure and the specific surface area of the biomasses. Same observations were noticed as the torrefaction temperature increases (as discussed earlier).

CONCLUSION

Jatropha has been touted as a clean and efficient global biofuel feedstock because of its many attributes; its biodiesel production capability, towering oil content, easy propagation, rapid growth, drought resistant nature, as well as its ability to thrive on any types of soil. Due to these lofty characteristics, researchers and policy-makers all over the globe have shown interest in pursuing Jatropha biofuel program. In this work, de-oiled seed kernel was thermochemically (albeit, pyrolytically) converted to hydrophobic-carbonised torrefied biomass with improved higher heating value which can be stored stably over time with low risk of mold, thus finds application as wood dust alternative upon densification or pelletization for domestic cooking and heating purposes. It can also act as charcoal in improved wood stoves to replace biobriquettes. Torrefaction has been identified as a promising technological possibility, in this regard. Commercialization of torrefied biomass has been achieved in developed nations, therefore Nigeria as a country should not fold her hands in embracing this technology to provide cheap and affordable torrefied biomass that can substitute wood dust for heating and cooking purposes for rural and urban dwellers.The current work substantiated torrefaction as an efficient thermochemical conversion process for DJSK. The following conclusions and observations could be drawn:

1. Increase in HHV was noticed as temperature increased from 200 °C to 300 °C. For the raw DJSK, the HHV were enhanced or enlarged by factors of 1.00, 1.17 and 1.46 at 200, 250 and 300 °C. Same observation was noticed in acid and alkali-treated samples. As the reaction temperature was amplified, the solid yield (%) of both raw and treated (acid and alkali) sample decreased. At 200 °C, the significant mass loss in solid yield gave rise to the expulsion of low molecular weight aromatic compounds
2. The FTIR results indicate that the –OH functional group was diminished in all samples, thereby leading to more hydrophobicity, increased HHV in the biomasses.
3. Morphological features of the raw and torrefied DJSK revealed the acid and alkali pretreatments at low concentration of 4 % caused surface damage with porous structure, which may likely be responsible for improved HHV. Surface morphological studies revealed that acid and alkali pretreatment enhanced the biomass surface structure as well as biomass specific surface area.

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